

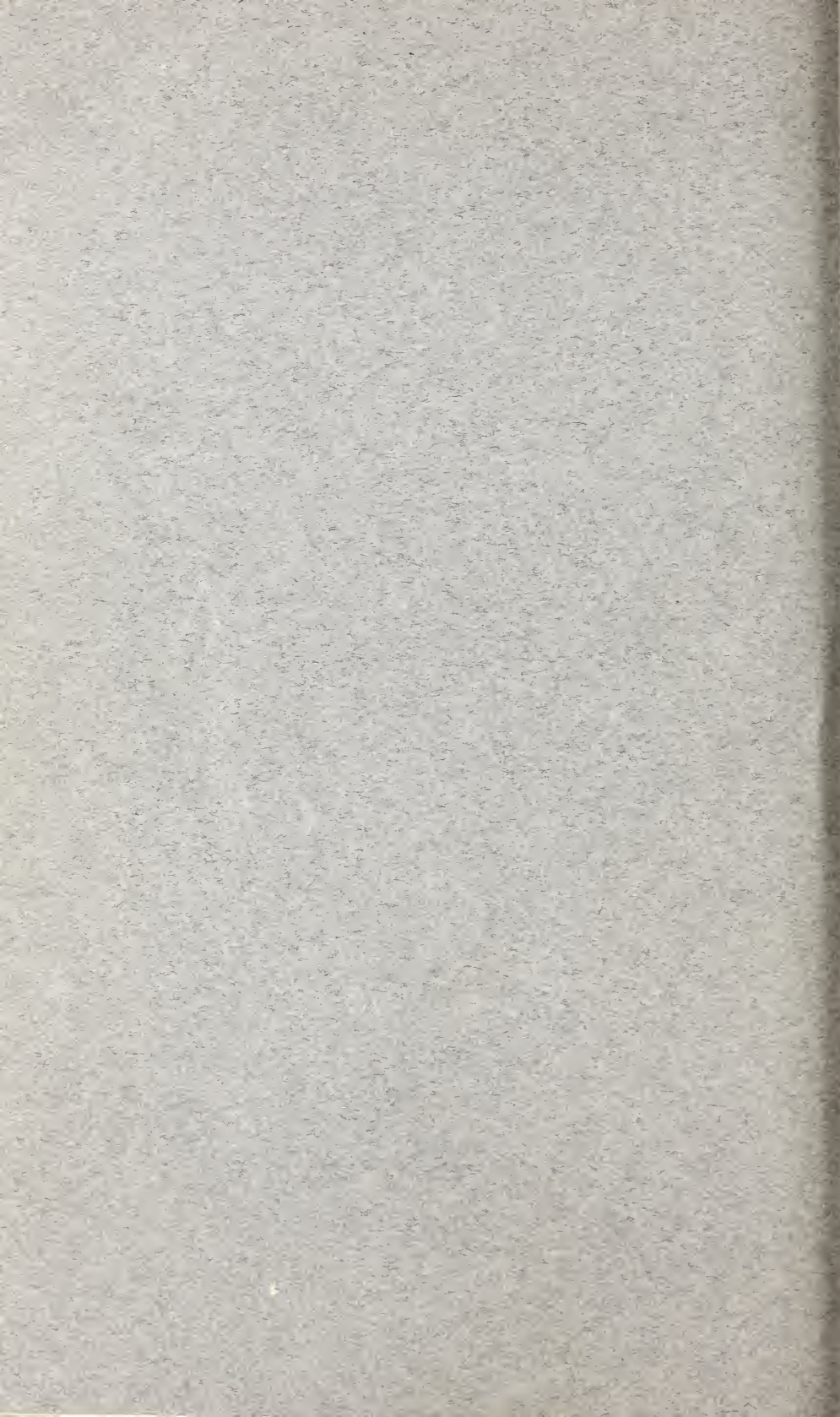
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**THE MAKING OF MIRRORS
BY THE DEPOSITION OF METAL
ON GLASS**

CIRCULAR OF THE BUREAU OF STANDARDS, No. 389



U. S. DEPARTMENT OF COMMERCE

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ISSUED JANUARY 6, 1931



UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1931

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ABSTRACT

This supersedes Letter Circular No. 32, Methods of Silvering Glass, and deals principally with the methods for producing mirrors by the chemical deposition of silver on glass. The Brashear, Rochelle salt, and formaldehyde formulas are given, together with a detailed discussion of the precautions which should be taken to avoid danger, and the technique which has been found to yield the most satisfactory results at the bureau. Methods are also given for the production of reflecting films on glass by the chemical deposition of copper, platinum, or lead sulphide, by cathode sputtering, and by the condensation of vaporized metals.

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I. INTRODUCTION

This publication supersedes Letter Circular No. 32, a collection of formulas for the preparation of silver on glass mirrors which was prepared to serve as a reply to the numerous requests for instructions concerning the preparation of mirrors. The frequency of these inquiries has increased. During the past two or three years their number has been particularly large because of the stimulus to the

construction of reflecting telescopes by amateurs through the work of Ingalls,¹ Porter, Ellis, and others. As a result, Letter Circular No. 32, in mimeograph form, has gone through a large number of editions, in the course of which many additions have been made, based either on the growth of the bureau's experience in making mirrors or on the requests for additional information received from our correspondents.

The present publication is a more complete revision with the scope of the subject matter enlarged to include the preparation of mirrors from materials other than silver and by processes other than chemical deposition. It deals principally, however, with the preparation of mirrors by the chemical deposition of silver on glass as this is the method of greatest importance for either scientific or commercial purposes. To the beginner this process offers certain difficulties which ordinarily vanish with experience, but which, nevertheless, necessitate a more or less definite period of apprenticeship. In order to shorten this period to a minimum, the technique of preparing the solutions has been described in great detail.

Silvering is not usually considered a dangerous procedure, but it is deemed wise to introduce the subject by a discussion of the incident dangers. The bureau's experience and the instances referred to in the body of this paper emphasize the need for certain stated precautions and indicate that one is taking an entirely unnecessary risk, probably greater than is commonly realized, in silvering without goggles.

Three different formulas for depositing silver are given: (1) The Brashear process in which the silvering solution contains potassium hydroxide as well as ammonium hydroxide with sugar as the reducing agent, and processes employing (2) Rochelle salt, and (3) formaldehyde, respectively, as reducing agents. Reference is then made to methods for the chemical deposition of copper, platinum, and lead sulphide for producing reflecting surfaces. Processes are also given for the production of mirrors by cathode sputtering and by the distillation of a metal to the surface which is to be made reflecting. These last two methods serve only for the production of relatively small mirrors, but are of considerable importance in connection with the preparation of apparatus for scientific research.

II. THE CHEMICAL DEPOSITION OF SILVER ON GLASS

1. THE PREPARATION OF THE SILVERING SOLUTION

(a) DANGERS ASSOCIATED WITH THE SILVERING SOLUTION

In all methods commonly used for the chemical deposition of silver on glass the silver is in an ammoniacal solution prepared by adding ammonium hydroxide to a solution of silver nitrate, and the silver is subsequently precipitated in the metallic form by the addition of a suitable reducing agent. In this solution compounds may be formed which are violently explosive and which detonate as a result of the slightest mechanical disturbance. At times these explosive compounds have formed with serious consequences during the process of silvering glass and instances are recorded² in which explo-

¹ Amateur Telescope Making, Albert G. Ingalls, editor. Published by Scientific American Publishing Co., New York; 1928.

² Centralz. f. Opt. u. Mech., 49, pp. 73-75; 1928.

sions of this nature have resulted in loss of sight through the action of ammonia on the eyes or have been sufficiently violent to produce considerable property damage. These explosions seem more likely to occur when using a formula in which potassium hydroxide is one of the constituents of the silvering solution as in Brashear's method. It seems, however, that they are possible occurrences with any of the methods of silvering. Less concentrated solutions greatly decrease the probability of explosions and the bureau's experience has shown that the formulas given herein do not produce explosive mixtures if the stated precautions are taken. Explosions are very likely to occur if the residue remaining after silvering is allowed to become dry or if empty vessels in which the silvering solution has been prepared or stored are allowed to dry without first having been carefully cleansed. Consequently, all vessels containing silvering solutions should be carefully cleaned immediately after use and all residues remaining from the silvering should be washed down the sink or otherwise safely disposed of without delay. If silvering is done regularly and on a large scale it becomes advisable to save all residues for the recovery of the silver. In such case sufficient hydrochloric acid should be added to all spent solutions and residues to acidify them. This precipitates the silver and also removes all danger of explosion.

Furthermore, bottles containing the silvering solution should be kept tightly corked when not in use to avoid the possibility of lowering the level by evaporation and the formation of a dried residue on the side walls. It is further recommended that the silvering solution for the Brashear process should not be stored, but prepared only as required. There is no danger associated with the reducing solution and it can be conveniently prepared in relatively large quantities as it does not deteriorate with age. Even after taking all recommended precautions it is considered advisable that the operator should always wear goggles for protecting the eyes when handling the silvering solution.

(b) THE CHOICE OF CHEMICALS

All chemicals used in the preparation of the solution must be of high purity as the use of impure reagents will very probably result in failure. The grade of chemicals known to the trade as C. P. will be found satisfactory. The use of distilled water is recommended, but if this is not available rain water may be tried, and in some localities it will be found that water from the tap may be used without detriment. A test may be made on a small mirror or, if the solution turns a light blue or pink when the silver nitrate is dissolved in water, it may be concluded that the latter is probably too impure for the purpose. The merest trace of chlorine, free or in combination, will cause failure. Consequently, when silvering small mirrors for which small amounts of solution are used, care must be taken that the solutions are not contaminated by the salt present in the natural perspiration of the hands.

Pure grain alcohol, required in some of the formulas, is difficult to obtain. Alcohol denatured by the addition of wood alcohol, 1 part in 20, may be used to replace the grain alcohol. This is alcohol denatured in accordance with special denaturing formula 3A of the Bureau of Internal Revenue. With Brashear's formula a trial has

shown that the commercial rubbing alcohol, sold under the trade name "Alcorub," may be used with satisfactory results. It is probable that a similar substitution may be made in the other formulas which call for grain alcohol and that rubbing alcohol sold under other trade names will serve equally well.

For preparing the solutions the use of round bottom or balloon flasks is recommended. These flasks are readily cleansed, the process of the addition of ammonia to the silver nitrate solution, to be described below, can be easily observed and, when required, the solution may be heated in the flask without the necessity of transferring it to a second container. In preparing the solution, as in all parts of the silvering process, one must guard carefully against the introduction of foreign material. The flasks should be carefully cleansed by nitric acid or potassium dichromate solution, rinsed with tap water, and finally with distilled water until all traces of acid are removed. Metal vessels are, in general, to be avoided not only because there is danger of the solution reacting with them but also because they are more difficult to clean. If using very large quantities of solution it is probable that metal vessels lined with silver might be employed satisfactorily. Earthenware or enamelware vessels are suitable if used only for this purpose. Wooden vessels may also be used if well paraffined.

(c) THE ADDITION OF AMMONIA TO THE SILVER-NITRATE SOLUTION

In preparing the silvering solution aqueous ammonia is added to the silver-nitrate solution in quantity just sufficient to redissolve the precipitate first formed. An operation of this sort, which is characteristic of each of the formulas to be given, is the most important step in the preparation of the solution. A relatively small excess of ammonia will prevent any deposition of silver and too little ammonia will result in an excess of precipitated silver oxide which is undesirable and must be removed by filtering. To insure the addition of the correct amount of ammonia the following procedure is recommended. Solutions A and B are prepared in accordance with the formula to be used. (See pp. 5 to 8.) The ammonia, which should be C. P. and concentrated (specific gravity 0.88 to 0.90), is added to solution A in small portions, and after each addition the solution is well shaken. At first the amount of precipitate formed will increase greatly with each addition of ammonia. The successive processes of adding ammonia and shaking the solution thoroughly are continued until the precipitate begins to redissolve and the further addition of ammonia tends to clear the solution. As the solution becomes cleared the ammonia should be added more cautiously and the duration of the intermediate period of shaking increased in order to give each portion of ammonia full opportunity to redissolve the precipitate as completely as possible before additional ammonia is added. It is desirable to add the minimum amount of ammonia that will redissolve the precipitate initially formed, but it is better to finish with a solution in which there is an excess of silver rather than an excess of ammonia. Accordingly, after one has added to solution A what is judged to be the requisite amount of ammonia, solution B is added in small amounts following the procedure that was used when adding ammonia. If only the correct amount of ammonia has been added

the addition of a small amount of solution B will be followed by a darkening of the solution, resulting from the precipitation of silver oxide which will be permanent and will not disappear even if the solution is shaken thoroughly and allowed to stand for an hour or two. If, however, the ammonia has been added in excess the silver oxide will redissolve and the solution will clear. In this case one must continue to add solution B until the permanent darkening of the solution is secured. No attempt should be made to use a silvering solution until this darkening is obtained, even if it should be necessary to prepare an additional amount of solution B. If this procedure is followed a slight excess of silver is assured and the silvering solution is certainly in a condition to be readily reduced when used. The above-described precise method of determining the amount of ammonia to be added to the silver-nitrate solution is the procedure recommended when silvering is done at infrequent intervals, because in such cases there usually exists an uncertainty regarding the exact strength of the aqueous ammonia solution which is used. If, however, much silvering is being done and the solutions are prepared in large quantities the amount of ammonia to be added can probably be satisfactorily controlled by measurements of density and volume, and the delay incident to the titration process can be avoided.

(d) THE BRASHEAR FORMULA

The Brashear³ formula is probably used more than that of any other process for silvering the surfaces of large mirrors of reflecting telescopes and laboratory mirrors where a thick coat of silver is required and the reflection is from the front surface.

The reducing solution

	Metric units	English units
Distilled water.....	1 liter.....	Ounces ¹ 33.81
Tablet or granulated sugar ²	90 g.....	3.17
Nitric acid (specific gravity 1.42).....	4 ml.....	.14

¹ For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

² Rock candy was formerly specified. Tablet sugar is the purest sugar which can be readily purchased at the grocery store. A good grade of granulated sugar can be used with satisfactory results.

The reducing solution is boiled for five minutes and allowed to cool before using. It is preferably prepared in large quantity, as it does not deteriorate, and is said to improve with age. If it is to be stored, 175 ml of grain alcohol is added to the above amount, after cooling, as a preservative. The boiling may be omitted if the reducing solution is prepared one or two weeks in advance of time of use.

The silver-nitrate solution

	Metric units	English units
A. Distilled water.....	400 ml.....	Ounces ^a 13.52
Silver nitrate.....	20 g.....	.71
Potassium hydroxide.....	10 g.....	.35
B. Distilled water.....	30 ml.....	1.01
Silver nitrate.....	2 g.....	.07

^a For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

³ Brashear, *English Mechanic*, 31, p. 237; 1880; and Wadsworth, *Astrophys. J.*, 1, p. 352; 1895.

When preparing solution A⁴ the chemicals are added in the order given. The addition of the potassium hydroxide produces a large amount of precipitate which is later to be redissolved by the addition of ammonium hydroxide. For complete instructions concerning the addition of the ammonium hydroxide and solution B see pages 4 and 5. If the specific gravity of the ammonium hydroxide is 0.90, approximately 50 ml will be required for the amount of solution given in the formula. This quantity of silver-nitrate solution will suffice for approximately 800 cm² (125 in²) of surface although a greater amount of solution may be used if a particularly heavy film is desired. The silver nitrate and reducing solution are to be mixed immediately before application to the surface to be silvered. One part by volume of reducing solution is mixed with four parts of silver-nitrate solution.

(c) THE ROCHELLE SALT FORMULA

The reducing solution

	Metric units	English units
Distilled water.....	1 liter.....	Ounces ¹ 33.81
Silver nitrate.....	2 g.....	.07
Rochelle salt.....	1.7 g.....	.06

¹ For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

When preparing this reducing solution of silver nitrate in distilled water it is heated to the boiling temperature and the Rochelle salt added, after which it is stirred while boiling for five minutes. It is then filtered before cooling and kept in a dark bottle.

The silver solution

	Metric units	English units
A. Distilled water.....	100 ml.....*	Ounces ^a 3.38
Silver nitrate.....	10 g.....	.35
B. Distilled water.....	30 ml.....	1.01
Silver nitrate.....	3 g.....	.10

^a For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

⁴ The procedure for preparing the silver solution here given is different from that of the Brashear process as given by Wadsworth. (See footnote 3, p. 5.) In the older method the chemicals are mixed as follows:

	Metric units	English units
A. Distilled water.....	300 ml.....	Ounces 10.14
Silver nitrate.....	20 g.....	.71
A'. Distilled water.....	100 ml.....	3.38
Potassium hydroxide.....	10 g.....	.35
B. Distilled water.....	30 ml.....	1.01
Silver nitrate.....	2 g.....	.07

Ammonium hydroxide is added to A until the precipitate which forms is redissolved. Solution A' is then added, forming a precipitate of silver oxide which is then redissolved by the further addition of ammonium hydroxide after which solution B is added until the solution acquires a permanent slight darkening. Each addition of ammonia and the solution B is made in accordance with the instructions on pages 4 and 5. The method given in this circular dispenses with one stage; that is, the first addition of ammonium hydroxide, with considerable saving of time and no evident sacrifice in quality of product.

To solution A, concentrated ammonium hydroxide is added, in quantity just sufficient to redissolve the precipitate first formed, after which the required amount of solution B is added. If the specific gravity of the ammonium hydroxide is 0.90, approximately 10 ml (0.3 ounce) will be required for the above quantity of solution. Full information concerning the addition of ammonium hydroxide and solution B will be found on pages 4 and 5. The solution is finally diluted to 1 liter (34 ounces) and filtered. The silver nitrate and reducing solution are mixed in equal volumes immediately before they are applied to the surface to be silvered and the silvering may be done at room temperature although it will be found advantageous to have the surface to be silvered slightly warmer than the solution. The above quantity of solution will give a thick film of silver on approximately 400 cm² (60 in.²) of surface although for a very heavy coat more solution may be employed.

(f) THE FORMALDEHYDE FORMULA

The reducing solution

	Metric units	English units
Distilled water.....	ml 200	Ounces ¹ 6.76
Formaldehyde.....	40	1.35

¹ For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

The silver nitrate solution

	Metric units	English units
A. Distilled water.....	1 liter.....	Ounces ¹ 33.81
Silver nitrate.....	20 g.....	.71
B. Distilled water.....	100 ml.....	3.38
Silver nitrate.....	2 g.....	.07

¹ For solids and liquids the avoirdupois and fluid ounces, respectively, are to be used in this formula.

To solution A, concentrated ammonium hydroxide is added, in quantity just sufficient to redissolve the precipitate formed, after which solution B is added as required. If the specific gravity of the ammonium hydroxide is 0.90, approximately 10 ml (0.3 ounce) will be required for the above amount.

For silvering, 5 parts of the silver nitrate solution are mixed with 1 part of reducing solution immediately before application to the surface to be silvered. The silvering proceeds well at a temperature of approximately 20° C. (68° F.).

(g) RELATIVE MERITS OF DIFFERENT FORMULAS FOR SILVERING

Of the formulas which have been given, the Brashear and Rochelle salt processes are, perhaps, the most generally employed and are regularly used at the bureau for the production of mirrors. For reflecting telescopes and other applications, where reflection from the front surface is required, the Brashear formula is commonly recommended as giving a film of silver which is very thick, has a very high coefficient of reflection, and which adheres firmly to the glass, thus permitting

frequent repolishing. It has, however, been the experience at this bureau that equally heavy coats, which polish well and which are satisfactory for front reflection, can be obtained with the Rochelle salt formula. To test this more completely 12 mirrors were made, 4 by the Brashear method as modified and given in the text of this publication, 4 by the older method described in the footnote, and 4 by the Rochelle salt formula. In order that differences of color might be detected, the relative reflection coefficients were measured by Dr. W. W. Coblentz for wave lengths 365, 405, and 579 $m\mu$. For the different mirrors the measured values of total visible reflection showed no differences greater than the error of measurement. Furthermore, there was no evidence of selective reflection except in the case of two of the mirrors prepared by the Brashear process which showed a relatively greater falling off in reflection for the ultra-violet than did the other 10. This selective reflection could most probably be attributed to the difference in the thicknesses of the films.

2. THE PRODUCTION OF THE REFLECTING FILM

(a) CLEANSING THE SURFACE TO BE SILVERED

The silvering is best done in a shallow tray only slightly larger than the surface to be silvered. For a large mirror a tray made of wood and thoroughly paraffined may be used, or, if the glass to be silvered is sufficiently thick a band of paraffined paper tied tightly around the glass and "cemented" to the edge with a soldering iron is a serviceable device for retaining the silvering fluid. The tray which is to be used for silvering may also be conveniently used for cleansing the surface to be silvered. If the surface is old and has not been previously silvered or is greasy from handling it should be first cleansed with alcohol, ether, or some similar solvent. Following this it should be scrupulously cleaned with nitric acid. A swab may be made by winding absorbent cotton on the end of a glass spatula or glass rod, with sufficient thickness of cotton so that there is no danger of scratching the glass with the rod. With such a swab and pure nitric acid, to which a little distilled water may be added, every part of the surface should be cleansed. Considerable pressure must be used in rubbing with the swab, and no part of the surface should be allowed to become dry during this process. If any part dries it must be swabbed and cleansed again. To rinse off the nitric acid, ordinary water may be used at first, followed by distilled water. Finally the mirror is placed in a tray or other container and covered with distilled water until ready to silver. After having been cleansed no part of the surface to be silvered should be allowed to become dry until after the silver film has been completed.

After cleansing with nitric acid, many advise a second cleansing with a strong solution of potassium hydroxide, followed by the application of French chalk, and rinsing as above. The nitric acid alone, however, will be found sufficient, provided the cleansing is thoroughly done and plenty of pressure used in the swabbing. During the entire process of cleansing the glass great care must be taken to avoid scratching the surface. If a satisfactory mirror is to be produced, the deposit must be made on a highly polished surface entirely free from defects. The slightest scratch or mark will show on the finished mirror.

In commercial silvering many manipulators follow the cleansing with nitric acid by a vigorous swabbing with a saturated solution of

stannous chloride (SnCl_2), which is carefully rinsed off with warm water. This is regarded as an essential feature in many of the "secret processes" used in the trade. The application of stannous chloride is not necessary for the production of good mirrors. However, its use favors the production of a heavy deposit under conditions which otherwise would yield a thin, unsatisfactory film.

The mirror should not be touched with the hand any more than is absolutely necessary during the process of cleansing, and under no condition should the surface to be silvered be touched after the nitric acid has been applied. The use of rubber gloves is a great convenience. They are desirable not only for the protection of the hands, but also because they protect the solutions from contamination. If stains at the edges of mirrors are to be absolutely avoided, they are, perhaps, indispensable.

(b) THE APPLICATION OF THE SILVERING SOLUTION

It is probably preferable to support the mirror by its back in the tray with the surface to be silvered facing downward and approximately 1 cm from the bottom. The sediment formed during the process of silvering is thus prevented from resting on the finished surface. Very good silvering can be done, however, with the piece to be silvered resting on the bottom of tray with the side to be silvered uppermost. Large telescope specula are necessarily silvered in this position. After the final cleansing the mirror is placed in the position for silvering and the surface covered with distilled water to a depth of 1 cm.

The required quantities of the reducing solution and silver nitrate solution are measured into two beakers, then poured together, quickly mixed and promptly poured over the surface to be silvered. If the Brashear formula is used it is not necessary to pour off the distilled water already in the tray, provided that its volume does not greatly exceed the combined volume of silvering solution used. For the Rochelle salt or the formaldehyde formula the procedure is the same except that the distilled water is poured off the mirror immediately before applying the silvering solution. For these last two processes it is also advisable to have the surface of the mirror 2° or 3° warmer than the solution. This can be conveniently accomplished by pouring warm distilled water over the surface immediately before silvering.

As the silvering proceeds, a heavy black sediment forms in the solution. During the silvering the tray must be rocked continuously to prevent this sediment from sticking to the silvered surface. For the same reason some consider it advantageous to swab very lightly with loose absorbent cotton over every part of the mirror surface. If the solution is left on the mirror too long the surface will tarnish and, consequently, it is advisable to make preliminary tests in small beakers or drinking glasses in order to determine the proper time for the process. When looking at the surface to observe the progress of the operation it should not be exposed to the air for more than one or two seconds at a time.

A heavier coat of silver may be obtained by successive applications of silvering solution. If this is to be done the entire surface of the mirror must be kept wet until the process is finished. When the

silvering with one bath has proceeded to completion the spent liquid must be poured off and the surface kept covered with distilled water until ready to apply the next silvering bath. At the close of the process the spent solution should be removed quickly and the mirror rinsed thoroughly, first with ordinary and then with distilled water. If there is much "bloom" on the surface, it may be swabbed lightly with absorbent cotton while rinsing.

(c) DRYING AND POLISHING

After the mirror has been stood on edge to dry, any surplus water at the edges may be removed with blotting paper. For front surface silvering it is generally necessary to polish the mirror over the entire surface with circular strokes after it is perfectly dry. For this purpose one uses a pad formed of the softest chamois skin wrapped around a wad of cotton. A little of the best optical rouge is rubbed into the chamois skin.

(d) LACQUER OR VARNISH AS A PROTECTIVE COATING

For back surface silvering, as in ordinary mirrors for domestic use, the silver coat may be covered with one or two coats of ordinary shellac and later covered with paint or other protector.

A transparent covering is often useful for the protection of front surface mirrors. A suitable lacquer can be prepared by diluting a clear nitrocellulose lacquer with amyl acetate until the consistency is such that the fluid flows freely and uniformly over the surface when it is tilted to allow the excess lacquer to flow off the surface. Care must be taken not to have the coat of lacquer too thin or interference colors will appear. This process of protecting front surface mirrors, however, has not been found satisfactory when the best optical surfaces are desired.

(e) COPPER AS A PROTECTIVE COATING ON SILVER

To prepare the plating bath 100 g of copper sulphate are dissolved in 1 liter (3 ounces in 1 quart) of distilled water and filtered.

The mirror is removed from the silvering bath, rinsed in distilled water, and transferred to the plating bath without having been permitted to dry. It is placed with silvered side up on a sheet of copper of approximately the same size as the mirror. A satisfactory electrical contact between the surface to be coppered and the sheet of copper must be provided by the silver on the edges and back of the mirror. A second sheet of copper approximately the same size as the mirror serves as the anode and is supported parallel to and at a distance of 1 or 2 cm above the surface to be coppered. If the work is done at infrequent intervals, dry cells provide a convenient source of current for coppering small surfaces. The positive or carbon terminal is connected to the anode; the negative terminal to the copper plate on which the mirror rests. The electrical current is applied for two to four minutes with a current density of approximately 0.05 ampere to each square centimeter (0.3 ampere to each square inch). It is necessary that the current be carefully controlled. For this purpose a rheostat and ammeter should be included in the circuit. The copper should be deposited as a bright metallic coat giving some specular reflection. After completion of the plating, the mirror is removed from the solution, rinsed in running water, and allowed to dry.

If the current density is too great the copper will deposit in a granular form and will rub off easily, while with too small a current density the deposition will not be uniform. The copper layer formed by this method is very thin, but affords considerable protection. It is well to paint the copper with asphaltum varnish or shellac.

(f) THE HALF-SILVERED MIRROR

At times a semitransparent reflecting surface of silver on glass is desired. In such cases the use of the Rochelle salt solution is recommended and the silvering is preferably done in a tray with a glass bottom in order that the opacity of the mirror may be observed without removing the mirror from the tray. It is necessary in this work to be even more careful than usual with the initial cleansing of the surface. Small defects in the deposit which are masked by a thick layer of silver are objectionable in the transparent film. If equipped with the necessary apparatus it is usually easier to prepare the semitransparent layer by cathode sputtering (see Sec. V) than by a method of chemical deposition.

(g) SPECIAL TREATMENT FOR SURFACES WHICH SILVER WITH DIFFICULTY

It is sometimes found that old surfaces which have been exposed to the atmosphere for a long period of time do not silver evenly. If a good optical surface is desired the only remedy is repolishing to expose a fresh surface. If, however, an optically regular surface is not required, the surface may be treated with a 2 per cent solution of hydrofluoric acid for two or three minutes, after which the usual cleansing may be followed by silvering. Such a method may be used when making reflectors for lamps or when silvering the interior surfaces of hollow ware which can not be reached with a swab. The hydrofluoric acid treatment will not lessen the detrimental effect of scratches and must not be used on mirrors for reflecting telescopes or other precise optical work.

(h) THE THICKNESS OF THE FILM

A method devised by Fizeau⁵ is convenient for determining the thickness of a silver film. A very small crystal of iodine is placed on a flat surface and the glass bearing the silver film to be measured is supported so that the film is 1 or 2 mm above the crystal. After a few minutes the iodine vapor will convert the silver immediately above the crystal into silver iodide, thus producing a transparent spot in the film. Neighboring portions of the film will be partially converted into silver iodide and, as a result, when the film is viewed by reflected light the transparent spot is seen surrounded by a series of concentric colored rings corresponding to the variations in thickness of the layer of silver iodide. It is essential that the film be exposed to the iodine until the central part of the pattern is transparent. A longer exposure will increase the size of the pattern, but will not increase the number of rings. The number of rings present is a measure of the thickness of the silver iodide at the center of the pattern, and this in turn is a measure of the amount of silver originally present; that is, a measure of the thickness of the film. To determine the thickness of film, the

⁵ *Annales de Chimie et de Physique*, 63, p. 385; 1861. See also Meslin, *Annales de Chimie et de Physique*, 29, p. 56; 1890.

number of concentric ring systems is counted and reference is made to the table given below.

Number of rings	Thickness $\times 10^6$
	<i>mm</i>
2-----	31
3-----	61
4-----	92
5-----	123
6-----	154
7-----	215

These values are derived by computations based on the relative densities of silver and silver iodide and on the refractive index of silver iodide.

If it is not convenient to invert the mirror over the crystal of iodine, the crystal may be laid on the silver film and a small beaker inverted over it to shield it from air currents. This, however, does not yield the symmetrical pattern which is obtained when the iodine does not actually touch the silver film.

The thickness of a silver film may vary from $30 \cdot 10^{-6}$ mm for a very thin film to approximately $200 \cdot 10^{-6}$ mm for a very thick film.

III. THE AMALGAM MIRROR

Mirrors were formerly made in which the reflecting surface was of glass backed by an amalgam of mercury and tin. Mirrors of this type, however, have been almost entirely supplanted by mirrors of silver on glass prepared by the methods described above because the mercury fumes present during the preparation of the amalgam mirrors were very injurious to the health of the workmen. Directions for the preparation of amalgam mirrors and for the repair of amalgam mirrors which are partially damaged by spots in the coating will be found in the Scientific American Cyclopedia of Formulas, edited by Albert H. Hopkins and published by Munn & Co., New York, N. Y.

IV. THE CHEMICAL DEPOSITION OF OTHER METALS ON GLASS

1. THE CHEMICAL DEPOSITION OF COPPER

In a manner similar to that described for silver, copper may be deposited on glass from a cupra-ammonium solution by a suitable reducing agent. Chattaway⁶ published a method for the deposition of copper in which phenylhydrazine is the reducing agent. It appears that this process is satisfactory for the deposition of copper on blown surfaces, as the interior surfaces of chemical glassware, but is not suitable for producing a good reflecting surface on a glass surface which has been ground and polished. French⁷ describes a modified method, using hydrazine sulphate as a reducing agent, by which mirrors of good optical quality have been produced.

⁶ Proc. Roy. Soc. London, 80A, pp. 88-92; 1907.

⁷ Trans. Opt. Soc. (London), 25, pp. 229-239; 1923-24. See also Barnard, Sci., 66, p. 330; 1927; and Eyber, Chem. Zeit., 51, p. 4; 1927.

2. THE CHEMICAL DEPOSITION OF GOLD

Draper⁸ describes a method by which a film of silver may be partially converted into a gold film by immersing the silvered mirror in a bath of gold chloride. The bureau has not succeeded in producing satisfactory reflecting surfaces by this method.

3. THE CHEMICAL DEPOSITION OF PLATINUM

McKelvey and Taylor⁹ describe a method for the deposition of platinum on glass from a colloidal solution. To prepare the solution 1 part of pure neutral platinic chloride, prepared by evaporating a 10 per cent solution to dryness, is moistened with a few drops of absolute alcohol and ground finely in an iced mortar with 10 parts of lavender oil, the latter being added gradually in small quantities. This solution is applied to the slightly warmed surface which is to be platinized and flowed into a film which is then heated carefully to drive off the volatile material, and finally heated to an incipient red heat to burn off the carbonaceous material and fuse the platinum into the glass. This method is not recommended for the preparation of reflecting surfaces, but is of value for the production of films on glass to which metal can be attached by soldering. For a reflecting surface of platinum, cathodic deposition (see p. 14) is superior.

4. THE CHEMICAL DEPOSITION OF LEAD SULPHIDE

Recently there has been some commercial demand for dark-colored mirrors. The following instructions for preparing such mirrors of metal sulphide are translated from an article by O. Hauser and Ernst Biesalski.¹⁰ This method has been tried at this bureau and found to yield a satisfactory reflecting surface.

Simple Preparation of Metal Sulphide Mirrors

By chance during a research we discovered that thiourea undergoes decomposition by alkali in water and alcohol solution at ordinary temperatures by which, among other things, H_2S is given off. If this decomposition takes place in the presence of the salt of a heavy metal its sulphide is precipitated upon the glass with a faultless mirror surface. By this method one can make sulphide mirrors on glass of any desired size without difficulty. This is particularly true for lead salts.

Preliminary experiments have shown that such mirrors can be used as electric resistances of small dimensions with a relatively high resistance, and they are, perhaps, useful for other purposes. We give the following formula for the preparation of a 9 by 12 cm glass plate. One supports it upon four bits of paraffin in a suitable developing tray and flows over the plate a solution of 1 g of thiourea in 50 to 75 ml of water, adds 50 to 75 ml of a dilute solution of lead acetate and finally 25 ml of dilute potassium hydroxide or ammonia solution, mixing continuously. Immediately the white lead hydroxide becomes dark and after a short time is all changed into black lead sulphide, and a firm, uniform, and deeply black metallic sulphide mirror forms in half an hour, first upon the lower and then upon the upper side of the glass plate. For larger plates a somewhat longer time is required. Without further treatment it is then washed with water and dried. To see the mirror surface one rubs the deposit off the upper surface of the glass plate.

⁸ Smithsonian Contributions to Knowledge, 34, p. 5.

⁹ J. Am. Chem. Soc., 42, pp. 1364-1374; 1920.

¹⁰ Chemiker Zeitung, 34, p. 1079; 1910.

V. THE DEPOSITION OF METALS BY CATHODE SPUTTERING

This method for the preparation of reflecting surfaces is particularly useful as a process for half-silvering and for depositing metals other than silver. Platinum is easily applied in this way and a surface is obtained which, while not so good a reflector as a freshly deposited silver surface, is largely free from any tendency to tarnish, even when used as a front surface reflector.

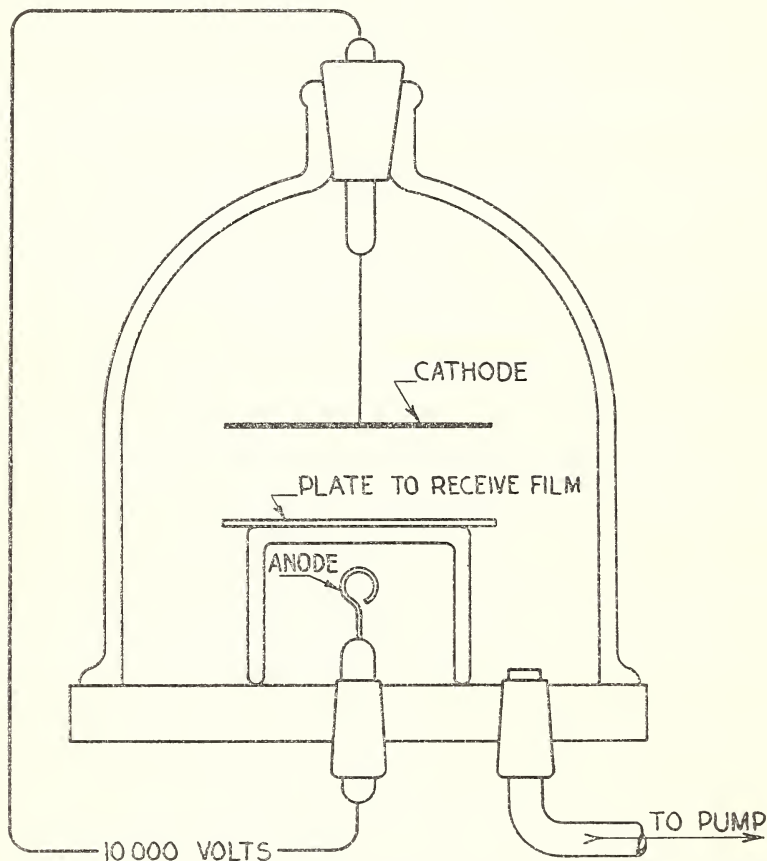


FIGURE 1.—Apparatus for the production of mirrors by cathode sputtering

The apparatus for this process is shown in Figure 1. The chamber which must be exhausted during the process of sputtering is made of a base plate of aluminum or glass and a glass bell jar with the joints made tight by soft wax. If an aluminum base plate is used it may serve as anode. The connection for evacuating is brought out through the base plate and the pressure must be reduced to approximately 0.001 mm. The cathode, which should be a thin sheet or wire grid of the metal to be deposited, and the surface to be coated should be parallel, approximately 25 mm apart. A 10,000-volt transformer (one-eighth kilowatt is satisfactory) furnishes the

current; and it is advisable, although not absolutely necessary, to rectify the current, either by kenotron or by a simple mechanical rectifier driven by a synchronous motor. If no rectifier is used the anode should preferably be of aluminum.

The initial deposit from a new cathode plate is sometimes not satisfactory because of foreign material present on the plate which is thrown down. Consequently it may be necessary to discard the first mirror which is prepared. In another method which has been successfully tried, the surface to receive the film is covered with a piece of paper attached to an iron armature. The paper protects the surface and is allowed to receive the initial deposit, after which it is withdrawn by a magnet acting on the armature through the walls of the bell jar. For cathode sputtering the surface should be thoroughly cleansed in the same manner as for chemical deposition.

Nutting¹¹ has produced by cathode sputtering mirrors as large as 28 cm (11 inches) square with the transmission equal to the reflection. Regarding his method he says that a 41 cm (16-inch) bell jar (cheese cover) was placed on a heavy plane base plate about 51 cm (20 inches) in diameter and 76 mm (3 inches) thick, specially made by the Pittsburgh Plate Glass Co. The 28 cm (11-inch) platinum cathode was laid on a sheet of glass supported by 25-mm (1-inch) posts on the base plate and discharged upward on to the plate to be coated which was supported on posts about 51 mm (2 inches) above it. The cover was pierced for the electrical connections (from a 10,000-volt transformer), the exhaust tube of pump, and the gas inlet. For joint grease a special solution of crude rubber in lard was made.

The obtaining of good mirrors was found to be largely a matter of keeping the (hydrogen) gas pressure carefully regulated so that the dark space just reached the mirror at all times. Some quantitative results (which served as a guide in timing the apparatus) are given in volume 2 of the Abridged Scientific Publications from the Research Laboratory of the Eastman Kodak Co., 1915-16.

Many metals can be deposited by this method. Platinum, gold, silver, or copper can be deposited without great difficulty. Aluminum is deposited very slowly, and it is for this reason that its use for a base plate is recommended when depositing other metals.

VI. THE DEPOSITION OF METALS BY EVAPORATION

This method of deposition has not been widely tested, and its possibilities are, therefore, little known, but it would seem to be especially valuable for small work where films of any readily volatile substances are required.

A convenient arrangement, which has been used by W. W. Nicholas at the Bureau of Standards, is shown in Figure 2. The material to be evaporated is placed inside a (say $\frac{1}{4}$ mm) tungsten coiled filament (*B*), which is clamped by strips of iron (*D*) to heavy tungsten wires (*C*) (say 1 mm). The material to be coated (*E*) is placed on a glass plate (*F*) supported on a clamp which can be raised or lowered to provide for various distances between *A* and *E*. If *E* is too close to *A*, the films will not be uniform, being thickest in the center.

¹¹ Privately communicated.

Also the heat from the filament might conceivably break the glass if this is thick and too close to the filament. The progress of the evaporation can be seen by looking up toward the filament from the bottom of the tube; this is especially convenient when semitransparent deposits are required. The (pyrex) glass tube (*G*) may be made entire, then cracked off at *H*, and subsequent sealings be accomplished with sealing wax.

With this apparatus opaque films on glass have been made of iron, copper, silver, gold, lead, tin, and aluminum. Probably many other metals which vaporize below the melting point of tungsten, as

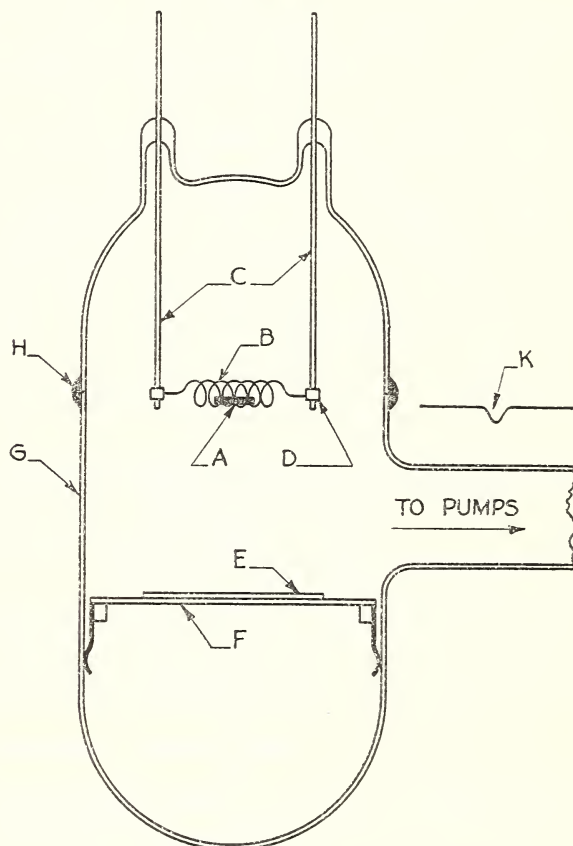


FIGURE 2.—Apparatus for the production of mirrors by the evaporation of metal

well as volatile compounds, may be deposited similarly. An alternative form for the tungsten filament is shown at *K* in Figure 2; a small piece of the metal to be evaporated is hung in the U-shaped segment. This form of filament, however, seems not to give such uniform films as the coiled form, and also small particles of metal are seen to be thrown off the molten globule. Some difficulty has been experienced with breakage of the tungsten filament, especially when aluminum is being evaporated; this may be due to the formation of brittle alloys.

A mercury vapor pump with liquid air trap, supported by a Hyvac oil pump, has usually been used to attain a high vacuum, but the Hyvac alone (pressure about 0.001 mm Hg) is sometimes sufficient (with lead and tin). With gold and zinc, however, a slight amount of air in the tube is sufficient to cause a black deposit.

J. E. Henderson, working at Yale,¹² evaporated from a tungsten filament nickel which had been electroplated onto the wire; the purpose of this technique was to secure especially uniform films.

Experiments in which small amounts of silver were evaporated from a molybdenum trough are described by D. L. Webster and others.¹³ For the production of very uniform and highly reflecting silver mirrors without polishing, it was found that the silver should be evaporated quite rapidly.

A. H. Pfund¹⁴ describes the evaporation of bismuth from a tungsten spiral. At pressures of 10^{-4} mm Hg the deposit was metallic and highly reflecting; at 0.25 mm Hg, however, a black film was produced having a very low coefficient of diffuse reflectivity.

WASHINGTON, August 6, 1930.

¹² His work was not published.

¹³ Proc. Nat. Acad. Sci., **14**, p. 679; 1928.

¹⁴ Washington meeting of American Physical Society; April, 1930.



